Revised manuscript submitted to *Sensors and Actuators B* after refereeing, January 2002.

PIEZOELECTRIC CHEMICAL SENSORS BASED ON MORPHOLINE CONTAINING POLYMERS

Gareth J. Price*, Andrew A. Clifton, Veronica J. Burton and (the late) Thomas C. Hunter

Department of Chemistry, University of Bath, BATH, BA2 7AY, United Kingdom.

* Address for correspondence and proofs. Tel: 01225 826504, Fax: 01225 826504
e-mail: g.j.price@bath.ac.uk.

ABSTRACT

A Quartz Crystal Microbalance, QCM, based system has been developed for the selective analysis of Cu^{2+} ions in aqueous solution. The crystal is coated with a thin film of poly(acryloyl morpholine) which selectively chelates Cu^{2+} over other M^{2+} ions. A novel coating procedure involving the preparation of sulphur terminated polymer chains followed by self-assembly onto the gold was used. The sensor could be used over the concentration range between 0.5 – 70 ppm. The method shows promise although further optimisation of the coating procedures and ligand loading are needed to extend the concentration range and improve the speed of response.

Keywords: Quartz crystal microbalance; chemical sensor; molecular recognition; selectivity; poly(acryloyl morpholine)

INTRODUCTION

The development of new chemical sensors that are specific for particular chemical species is an active area of research. Amongst the various type of sensor available, there is considerable interest in piezoelectric sensors [1 – 3], often known as a *quartz crystal microbalance, QCM*. Application of an alternating voltage to the gold electrodes plated onto a quartz crystal results in oscillation at a fundamental resonant frequency [4]. The principle of the microbalance is that, within certain limits, this frequency varies linearly [5] with an applied mass, M, according to the Sauerbrey equation, (1).

$$\Delta F = (F_o^2 / A\, N\, \rho_q)\, M \qquad \textbf{(1)}$$

where F_o is the fundamental oscillation frequency of the quartz crystal (in this work 10 Mz), A is the active area of the gold, *N* is a constant for the particular grade of quartz and ρ_q is the density of quartz.

While it is well known that Equation (1) is at best an approximation, it is adequate so long as the frequency change is limited to < 0.02 F_o and the fluid in which the crystal operates causes low acoustic loss. Greater absolute accuracy can be achieved by measuring the impedance changes across the crystal rather than the simple frequency change [6, 7] but for straightforward work, particularly where the system may readily be calibrated, the Sauerbrey equation is satisfactory.

Substitution of appropriate values into Equation (1) gives a mass sensitivity in the sub-nanogram range. This high mass sensitivity has been exploited in a range of sensors for gas and vapour phase work [8 - 10] but more recently, applications have been developed for use in solution despite the lower resolution caused by the viscous damping of the resonance by the liquid. Some recent examples of such uses include immunoassays [11], electrochemical analysis [12], ion binding studies [13], interactions in biomaterials [2] and determination of trace dissolved organics [14, 15].

The major drawback of the QCM is a lack of selectivity since there is no discrimination between the source of the mass changes. There are a number of approaches to provide the microbalance with chemical sensitivity, including coating the crystal with responsive materials such as amines to interact with carbon dioxide [16] or, more recently, molecularly imprinted polymers [17]. Our approach [18, 19] has been to use functional polymers which recognise only one or a very limited range of chemical species. In the gas phase, this can be achieved simply by coating the crystal with polymer and the approach has been used with success by other workers. The object of our current work is to analyse for metal ions in solution, necessitating a modified approach for the use of polymers containing chelating ligands. Particular requirements of such systems include a high loading of chelating ligand to ensure good sensitivity as well as rapid mass transfer. This can be achieved by using a coating that is highly compatible with the solvent so that it swells and allows solvent and analyte to permeate through. To prevent the coating from dissolving, it can be crosslinked although anchorage to the crystal via covalent bonds would give better long-term stability. It is well known that sulphur containing moieties can self-assemble and be irreversibly attached to clean gold surfaces [20, 21]. Thus, in this work, chelating polymers terminated with sulphur groups have been prepared and permanently attached to the quartz crystals.

For this study, morpholine containing compounds were chosen as the chelating ligand as these have been shown to selectively chelate Cu^{2+} ions [22] in aqueous solution. Previous work [17] indicated that the approach could be successful and morpholine containing polymer coatings gave QCM sensors with a high preference for copper ions. However, in that work the ligand loading achieved was rather low and the aims of this work were firstly therefore to investigate whether polymers containing larger amounts of morpholine could be synthesised and coated onto crystals and secondly to study their metal ion absorption capacities and potential sensor behaviour.

EXPERIMENTAL

Materials: N-acryloyl morpholine, NAM, (99%) was obtained from Lancaster Ltd. Other monomers, solvents and reagents were obtained from Aldrich Ltd. in the purest form available. Inhibitors were removed from the monomers by washing and/or passage through removal columns and were further purified by distillation at reduced pressure. The metal salts used as analytes were of Analytical grade (BDH Ltd.) Water was doubly distilled in glass apparatus before use.

Analytical methods: FTIR and NMR spectra were recorded on a Nicolet 510P and a JEOL GX400 spectrometer respectively. Gel permeation chromatography was carried out at Rapra Ltd. using a dimethyl formamide. Average molar masses are reported relative to poly(ethylene oxide) standards. Atomic Absorption Spectrophotometry, AAS, was carried out using standard methods on a Varian AA275 instrument.

Quartz Crystal Microbalance: The electrical circuit used to operate the QCM was constructed at the University of Bath and has been described previously [17]. In brief, the difference in resonant frequency between a working, functionalised crystal and a blank, reference crystal was measured and monitored using a circuit interfaced to a Personal Computer which was used for data collection and manipulation. The crystals were mounted in a holder that could be rapidly immersed in a container of stirred solution thermostatted to ± 0.1 °C. This typically gave a frequency response stable to within ± 5 Hz over several hours. The crystals used had a base frequency of 10.0 MHz with a gold coating of diameter 12.4 mm and were obtained from Euroquartz Ltd. (Crewkerne, Somerset, U.K.). To prevent electrolysis, the leads were insulated by coating with a non-conducting paint.

Polymerization methods: For polymerizations carried out to give soluble polymers for crystal coating, a typical procedure was as follows. To a solution of 1.0 g (6.5 mmol) NAM in 5 cm^3 water was added 0.5 mmol each of potassium persulphate and sodium metabisulphite. A high concentration of initiator was used to produce low molecular weight polymers. The solution was degassed by repeated freeze-thaw cycles and the ampoule heated to 60 °C for 1 hr. The mixture was poured into 50 cm^3 of ice-cold butan-2-ol to precipitate the polymer as a white powder that was recovered by filtration. Further polymerizations were performed by including 0.005 - 0.06 g 2-aminoethane thiol (as the hydrochloride salt) as a chain transfer agent in the expectation that chains terminated with sulphur containing moieties would be produced to aid attachment to the crystals.

In order to determine the absorption capacity and selectivity of the polymers, samples of solid powders were prepared by suspension polymerization using a method adapted from that of Epton *et al*. [23]. To a 1 L flask equipped with an overhead mechanical stirrer was added 300 cm^3 mineral oil with 5 cm^3 'Tween85' surfactant. This was stirred for 1hr at 50 °C while being purged with nitrogen gas. A solution of 10 g NAM, 0.75 g each of potassium persulphate and sodium metabisulphite and 0.4 g N,N-diallyltartardiamide in 60 cm^3 water was deoxygenated and added to the flask under vigorous stirring. The last compound was added to lightly crosslink the structure, preventing solubility. The insoluble material resulting from precipitation was ground to a fine (80 mesh) particle size.

Crystal coating: A new crystal was cleaned with methanol and chloroform before being dried at 105 °C. It was then immersed in a solution of the polymer under investigation at a concentration of 1 g in 30 cm^3 dimethyl formamide for 24 hr. After coating, it was washed in hot methanol and water to remove any physisorbed material until the crystal reached a constant oscillation frequency.

Selectivity testing: Aqueous standard solutions containing approximately 10 ppm of the sulphates of copper, nickel cobalt or zinc. 0.1 g of the crosslinked polymer powder was added and the mixture stirred at 25 °C for 24 hr. The polymer was recovered by filtration and the metal ion concentration of the solutions determined by AAS.

RESULTS AND DISCUSSION

In order to confirm that the polymer ligand would have the selectivity toward metal ions as in our previous work and to determine its absorption capacity, ~ 0.1 g samples of the lightly crosslinked powdered polymer prepared by suspension polymerisation were added to 20 cm^3 of solutions with initial concentration 10 ppm and shaken gently for 5 hr in a tube maintained at 25 °C. There was no change in the concentration of the $CoSO_4$ or $ZnSO_4$ solutions. The $NiSO_4$ solution changed from 10 ppm to 9.85 ppm while that for the copper sulphate was reduced from the initial value to 6.4 ppm. The level of absorption was therefore 1.5 mg Cu^{2+} (g resin)$^{-1}$. Calculation on a molar basis suggested that only one in approximately 300 of the morpholine groups was involved in chelating the Cu^{2+}, implying that little diffusion into the bulk resin was taking place despite the observed considerable swelling of the resin.

The kinetics of this adsorption were investigated by following the solution concentration with time after immersion of 16.2 mg of the poly(NAM) powder in 20 cm^3 of 10 ppm Cu^{2+} solution. The results are shown in Figure 1. They indicate that an initial adsorption is very rapid and complete within 1 – 2 min. Thereafter, only a small additional adsorption takes place. This is certainly consistent with only those sites on or close to the surface undergoing rapid adsorption and the majority of the functionality buried within the powder being unavailable for reaction.

Figure 1 near here

While these results are far from optimised, they do show that there is selectivity for Cu^{2+} over the other M^{2+} ions with this polymer so that sensor crystals were prepared from this material. In this application, the polymer film thickness was very much smaller so that it was anticipated that the kinetics should be much faster and diffusion effects less important.

A number of different protocols were used in an attempt to consistently produce a thin film coating on the crystal. An approach derived from previous work [17] involved coating the gold with a compound onto which the polymer can react. This was attempted using allyl mercaptan or thioctic acid to form films on the gold and the crystal was then immersed in the polymerizing solution. However, this was only partially successful in that polymer was certainly grafted to the crystal giving frequency changes of up to 5 kHz but, despite considerable variation of the experimental parameters (monomer and initiator concentrations, solvent, temperature etc.) the mass of coating was irreproducible and could not be controlled.

The most successful approach was to prepare the polymer chains with sulphur containing groups at their ends so that they could then adsorb onto the crystal from solution by self-assembly. This was achieved by carrying out the polymerization in the presence of sulphur containing chain transfer agents. Reaction with growing polymer chains would yield chains carrying the desired sulphur groups at their ends. Recovery of these polymer in a usable form was sometimes difficult and in some cases, only a gel resulted from which some soluble material could be extracted. This indicates that the reaction is not a straightforward polymerization but that there are side reactions taking place. Spectral analysis (IR, NMR) of the recovered soluble polymer fractions confirmed the expected structures. The aim of the reactions was to produce low molar mass materals and this is demonstrated by the average molecular weights shown in Table 1. It would be expected that inclusion of the chain transfer agent, 2-AET would lower the final molecular weight achieved. That this does not occur is also suggestive of the polymerization not taking place by entirely conventional means and this is under further investigation. However, for the purposes of this work, the polymers produced were satisfactory and were found to adsorb to the crystal.

The frequency changes occurring during the sensor crystal preparation are illustrated in Figure 2. The clean crystal had a resonant frequency difference, measured in dry air, from the blank crystal of 43420 Hz. Measurements over 100 s gave a standard deviation of $\pm$ 5 Hz. After coating with poly(NAM) from solution in dimethyl formamide, washing and drying, the frequency shift (also measured in air) changed to 44340 $\pm$ 4 Hz. For the size of crystal and grade of quartz used here, the mass sensitivity predicted by Equation (1) is 0.47 Hz ng^{-1}. Hence the frequency change implies that approximately 1.95 mg of polymer had been deposited, given the approximations involved in using the Sauerbrey equation. This corresponds to a film thickness of 10 $\pm$ 5 μm, the large uncertainty arising largely from the uncertain area and roughness of the crystal. Immersion of this coated crystal in water raised the frequency shift to 51748 $\pm$ 5 Hz due to the viscous drag and acoustic loss imposed by the liquid on the surface of the crystal. On adding Cu^{2+} to give a 20 ppm solution, the increase in frequency can readily be seen. A series of blank experiments was carried out with no polymer coating and the changes in frequency on adding the Cu^{2+} were not significant.

Figure 2 near here

To determine whether the selectivity determined for the solid resins was retained in the thin film on the crystal, the frequency change on exposure to various metal ion solutions was measured. A coated crystal was immersed in water and, when the oscillation frequency was stable, a solution of the metal ion added to bring the total concentration in the vessel to 20 mg dm^{-3}. Some results are shown in Figure 3. As expected, addition of Co^{2+} or Zn^{2+} resulted in no significant frequency change. Between each experiment, the crystal was removed and immersed for 5 min in 0.1 mol dm^{-3} EDTA solution and washed in water to remove any adsorbed ions before being re-equilibrated in water.

Figure 3 near here

Addition of Ni^{2+} resulted in a small frequency gain but this was much smaller than that for Cu^{2+}. The latter shows some variation in the four experiments and it was noticeable that, on repeated operation, the variation between consecutive runs became larger. One explanation for this is that not all of the adsorbed material from previous runs was removed so that some potential adsorption sites were blocked. There was no evidence (SEM, frequency changes) of changes to the polymer film nor of loss of material from the crystal. Improvement of this reproducibility is necessary before any commercial sensor could be used.

In order to determine the potential sensitivity of this sensor, successive additions of 1 ppm Cu^{2+} were added to the vessel with the results shown in Figure 4. In each case there was a rapid initial rise in frequency after which the response levelled out, although in some cases, a slow absorption continued. This indicates that there is a kinetic effect in operation which was often seen during testing. It is possible that some electrochemical effect comes into play but it is more likely that there is a distribution of ligand sites with some less accessible. Optimisation of the coating thickness should allow us to eliminate these effects. The plot of frequency change versus concentration is shown in Figure 5. Regression of the results (r = 0.98) gives a response of 103 $\pm$ 10 Hz ppm^{-1}. Given the characteristics of the apparatus described here, this would suggest that concentrations in the range of 0.2 - 0.5 ppm could routinely be measured. However, a more complete optimisation of the polymer structure and coating procedures should allow at least a five-fold improvement on this. This is similar to the values achieved in previous work so that the number of ligand groups would appear not to be the limiting factor. With the present apparatus, the maximum frequency change which could be achieved before losing the crystal oscillation was ca. 7.5 kHz, corresponding to an upper detection limit of approximately 70 ppm. Again, this should be improved by complete system optimisation. In addition, the effect of pH and other potential interferences needs to be quantified.

Figures 4 and 5 near here

Our previous approach was to prepare a copolymer where only part of the chains were functionalised to carry the chelating ligand. The expectation that polymers carrying very high ligand loadings – inherent in poly(NAM) – would lead to increased sensitivity has not been realised. Indeed, a new effect has arisen whereby the response is slower, presumably due to a wide distribution of ligand sites within the film giving a heterogeneous adsorption environment. The results reported here suggest that there is an optimum level for ligand loading beyond which no further increase in adsorption can take place. One method to improve the accessibility of the chelating groups is to include them in a highly porous film. Such films can be obtained by polymerization of microemulsions and this approach was described recently [24]. Further optimisation of sensor behaviour thus depends on careful tailoring of the structure and morphology of the polymer and the resulting film on the crystal. However, the results given here confirm previous work that demonstrates that the general approach adopted could be a useful one for further development of QCM sensors to be used in solution.

CONCLUSIONS

This work has shown that the approach of using functional polymers as coatings for a QCM can lead to useful sensors in aqueous solution. A Quartz Crystal Microbalance, QCM, based system has been developed for the selective analysis of Cu^{2+} ions in aqueous solution. A novel coating procedure involving the preparation of sulphur terminated polymer chains was used to prepare crystals coated with thin films of poly(acryloyl morpholine) which selectively chelated Cu^{2+} over other M^{2+} ions. . The sensor could be used over the concentration range between 0.5 – 70 ppm. Further optimisation, particularly of the precise ligand loading of the polymer and the film thickness is needed before a commercially available sensor could be developed but the approach offers a great deal of flexibility given the number of selective polymer extractants which are available.

While the approach here has involved a sensor for metal ions, the approach could be extended for a range of other analytes by using the principles of molecular recognition and this work is being persued in our laboratory. Examples are the use of cryptands to determine alkali metal ions [18] and the use of chiral polymers for the recognition and determination of enantiomers in mixtures.

ACKNOWLEDGEMENT

We are grateful to EPSRC for financial support of part of this work via grant GR/H11020**.**

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CAPTIONS FOR FIGURES

Figure 1: Uptake of Cu^{2+} from aqueous solution by crosslinked poly(N-acryloyl morpholine) resin

Figure 2: QCM frequency changes in preparing a poly(NAM) coated sensor crystal

� Uncoated crystal in air; O polymer coated crystal in air;

 polymer coated crystal immersed in water; ℓ addition of 20 ppm Cu^{2+}

Figure 3: QCM response to 20 mg dm^{-3} aqueous solutions of Cu^{2+} (←) Ni^{2+} () and Zn^{2+} (ℓ).

Figure 4: QCM response to successive 1 ppm additions (indicated by arrows) of $Cu^{2+}_{(aq)}$.

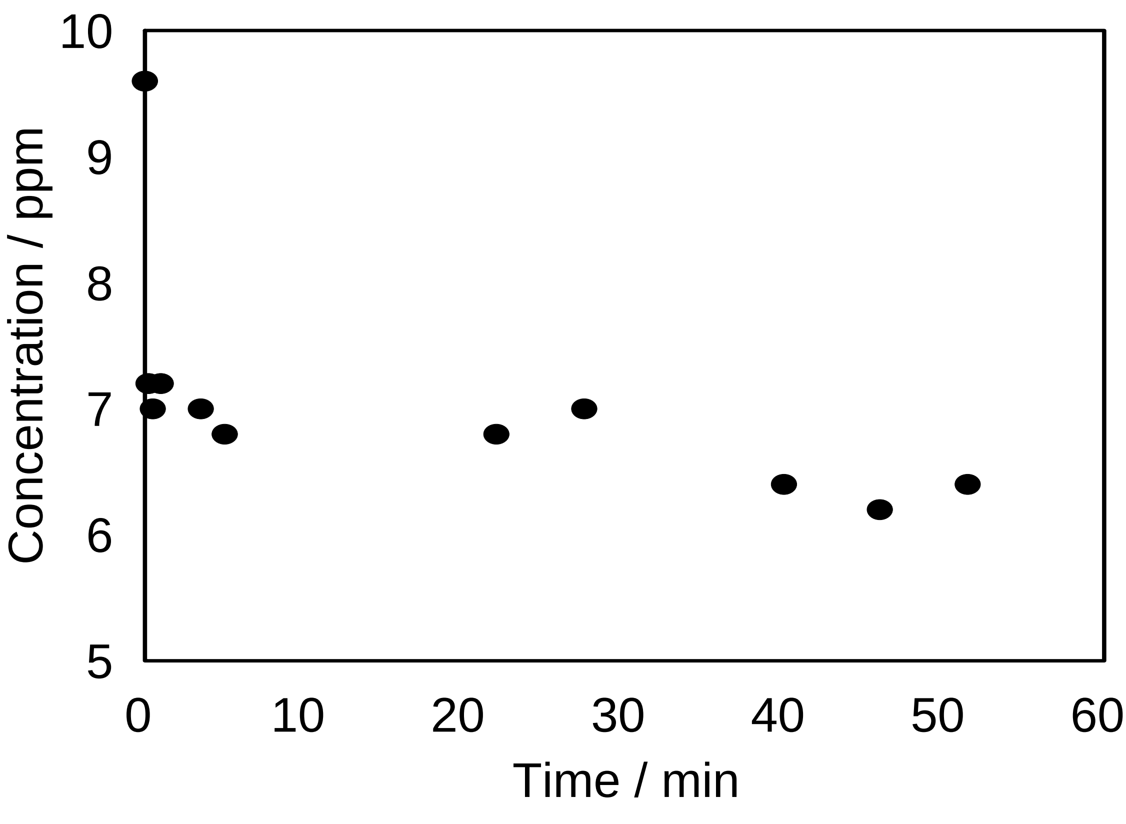
Figure 5: Calibration plot for QCM response to $Cu^{2+}_{(aq)}$.

Table 1: Molecular weights* of poly(N-acryloyl morpholine)

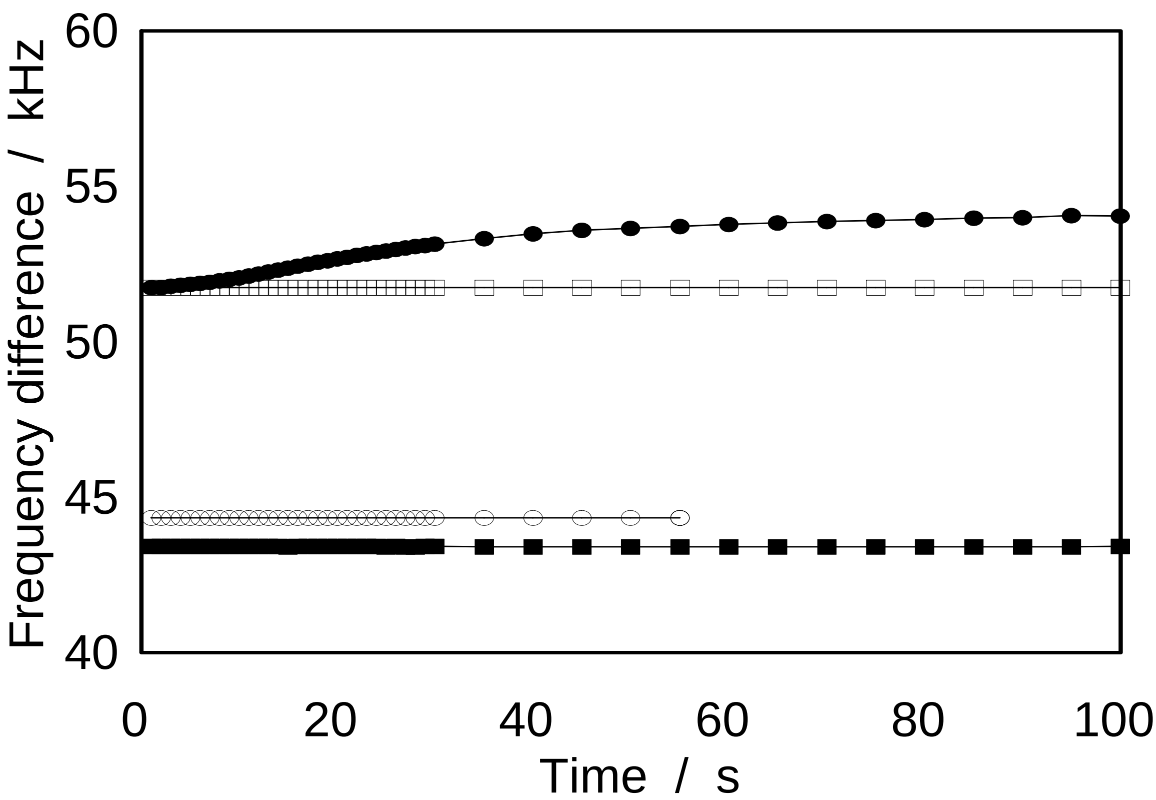
Polymer Code	NAM / mmol	2-AET / mmol	Number Av. Mol. Wt.	Polydispersity
1	20	0	5120	1.5
2	20	0.5	4330	1.7
3	20	1.8	3390	1.7
4	20	3.0	4310	2.4

* Relative to poly(ethylene oxide) standards.
NAM - N-acryloyl morpholine;
2-AET - 2-aminoethanethiol.

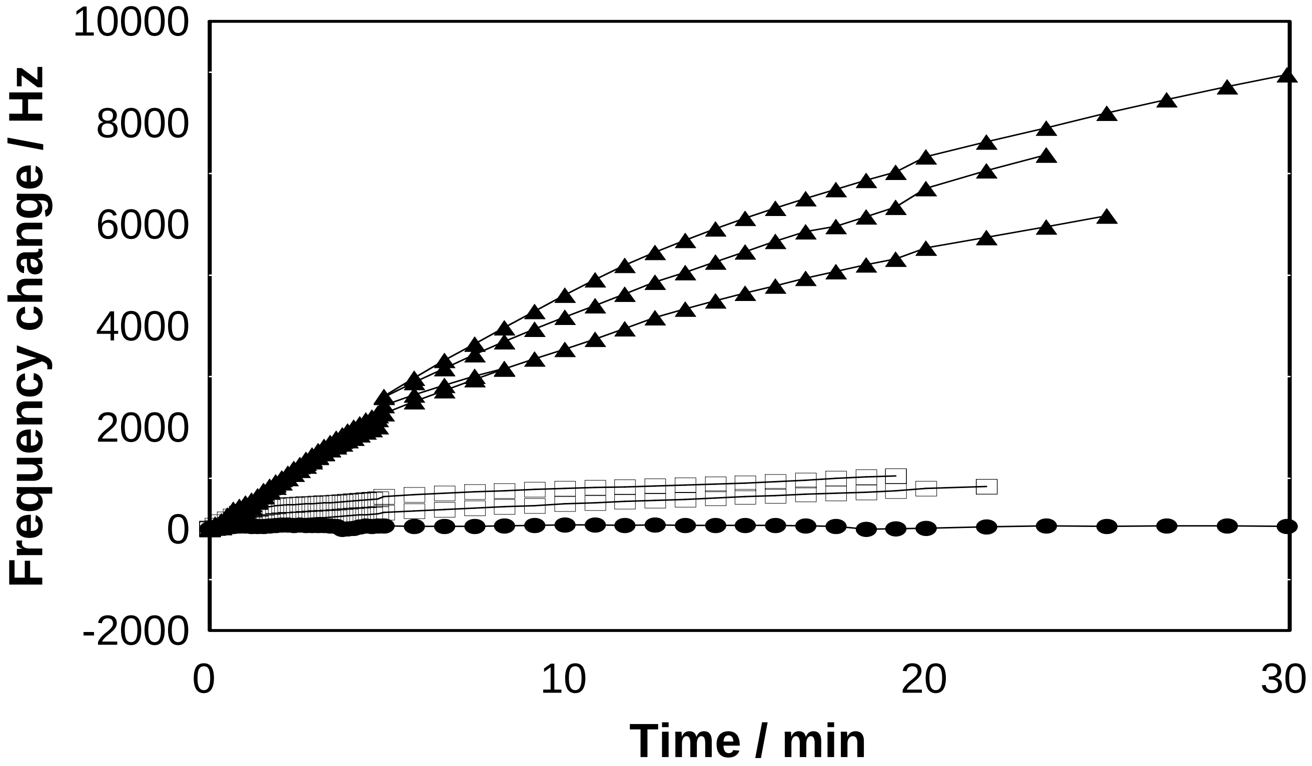
Price et al. Piezoelectric chemical sensors based on morpholine containing polymers Figure 1



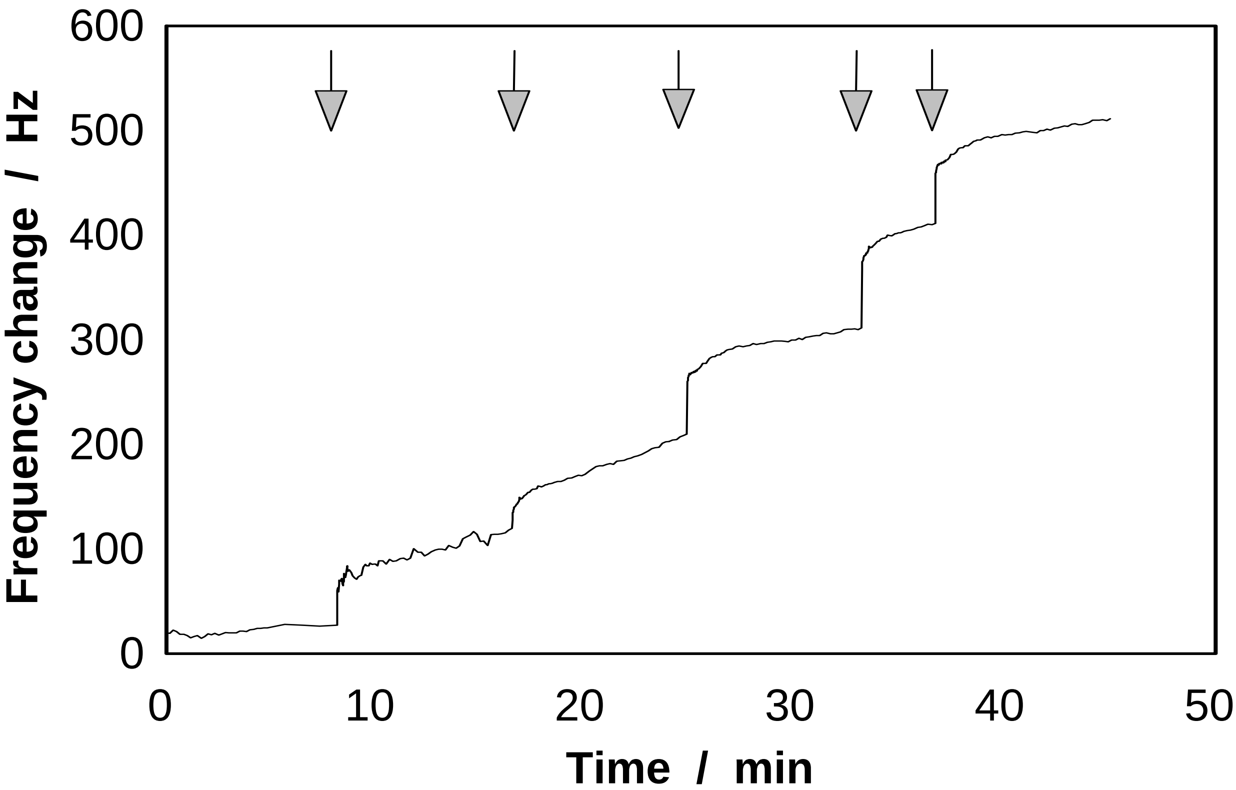
Price et al. Piezoelectric chemical sensors based on morpholine containing polymers Figure 2



Price et al. Piezoelectric chemical sensors based on morpholine containing polymers Figure 3



Price et al. Piezoelectric chemical sensors based on morpholine containing polymers Figure 4



Price et al. Piezoelectric chemical sensors based on morpholine containing polymers Figure 5